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Ionic Attachment as a Feasible Approach
to Heterogenizing Anionic Solution Catalysts.
The Carbonylation of Methanol

by

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Anton El A'mma and Alan Zombeck

ABSTRACT

Few definitive examples of ionically supported anionic transition metal complexes for use in catalysis have been reported, even though there are several advantages to be gained from such systems. To demonstrate the feasibility and usefulness of such materials in catalysis, we investigated the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalyzed carbonylation of methanol to acetic acid. The ionically supported $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ species was found to be equal in catalytic activity to the homogeneous complex, and leaching of the catalyst could be eliminated by suitable choice of solvent and resin/rhodium ratios. Additionally, we investigated the usefulness of a solid phase acid in catalyzing the formation of CH_3I from NaI (NaI by itself is inactive). We found this acid catalyst was active in this regard, and that the acidity was retained within the solid phase. These experiments suggest a general application of anion exchange resins as a mechanistic tool for detecting catalysis by anionic species in homogeneous processes.

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INTRODUCTION:

The advantages of heterogenizing homogeneous catalysts are well documented,⁽¹⁾ and numerous examples of the successful application of this concept to many different catalytic systems have been reported.⁽²⁾ Covalent attachment of the catalyst to the polymer support is generally utilized and examples of ionically bound polymer supported catalysts are seldom found. To date anion exchange resins have been used to support mononuclear transition metal ions such as PtCl_4^{-2} , PdCl_4^{-2} and $\text{RhCl}_4^{-2(2e)}$ for use as hydrogenation catalysts. A cation exchange resin has been used to support Rh_2^{+4} .⁽³⁾ More recently rhodium clusters have been supported on an Amberlyst A-21 resin⁽⁴⁾ (a polystyrene resin functionalized with N,N-dimethylbenzylamine groups). Neutral clusters were employed which underwent reaction upon attachment. It was proposed that ionic species formed in the reactions were converted to neutral rhodium-nitrogen adducts to account for the retention of the metal. The authors stated that they were uncertain about the identity of the active catalytic (hydrogenation) species. Presumably the lack of ionic systems is due to doubts about the lability of the ionic bonds in solution as well as concern about possible rate inhibiting effects resulting from increased charge delocalization on oxidatively adding a substrate to the catalyst. The small number of ionically supported systems reported encouraged us to attempt the preparation of such catalysts and to investigate the leaching characteristics of the materials.

There are several advantages in demonstrating the stability of ionically bound catalysts. Many transition metal catalyst systems involve ionic complexes that react with neutral, non-polar, substrates leading to problems with their mutual solubility in one solvent. Ionic attachment of the catalyst to a support has the advantage of dispersing the metal anions so that most of the catalyst in the swollen polymer is accessible to neutral, non-polar substrates. Additionally, ionic polymer supports may be of value in trapping ionic catalysts and inhibiting second order decomposition reactions. Capturing ionic solution catalysts and transferring their activity to a solid can provide an important tool for characterizing the charge of the catalyst in the solution reaction.

To demonstrate the feasibility and practicality of ionically binding catalysts we chose the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalyzed carbonylation of methanol to acetic acid. There were several reasons for choosing this particular system. First, the homogeneous reaction has been thoroughly studied,⁽⁵⁾ enabling us to start on a firm mechanistic ground. Second, the solvent system for this reaction is very polar, and contains several potential counter-ions which could conceivably substitute for the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ species, resulting in its leaching into solution. This feature allowed us to determine the practicality of ionically supporting a catalyst under the least favorable conditions. Third, the rate determining step of this reaction involves an increase in the coordination number of the catalyst,⁽⁶⁾ offering an opportunity to detect negative rate effects resulting from an increased ionic size. Fourth, several at-

tempts have already been made to heterogenize the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ species or other active rhodium species, and all have met with only limited success. The first example in 1969 involved using rhodium nitrate impregnated on activated charcoal.⁽⁷⁾ Similarly, a solution of $\text{Rh}(\text{CO})_2\text{I}_2^-$ was impregnated on charcoal by Roth et al. and was found to exhibit identical reaction order dependencies.⁽⁸⁾ Gates, et al. found extensive leaching of a covalently bound rhodium species.⁽⁹⁾ Catalysts showing activity for the carbonylation of methanol have been produced by incorporating rhodium into various zeolites.⁽¹⁰⁻¹²⁾ The most recent example, by Scurnell and Howe, produced a catalyst with comparable activities to the homogeneous case. Finally, the choice of this system gave us an opportunity to simultaneously investigate the effectiveness of a solid phase acid catalyst on the formation of the promoter, CH_3I , from sodium iodide (vide infra). Thus we feel the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalyzed carbonylation of methanol to acetic acid reaction is well suited for a demonstration of the feasibility and value of ionically binding a catalyst to a polymer support.

The mechanism of the homogeneous reaction is well understood (see Figure 1). A wide variety of rhodium catalyst precursors may be used, all of which form the active catalyst, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, in the presence of CO and I^- .⁽¹³⁾ This anionic species oxidatively adds CH_3I (promoter) as evidenced by infrared and product isolation.⁽⁶⁾ Kinetic studies indicate the oxidative addition of CH_3I to the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ species is the rate determining step; the carbonylation reaction follows the rate expression⁽¹³⁾ (eqn 1).

$$\text{rate} = k[(\text{Rh}(\text{CO})_2\text{I}_2)^-][\text{CH}_3\text{I}] \quad (1)$$

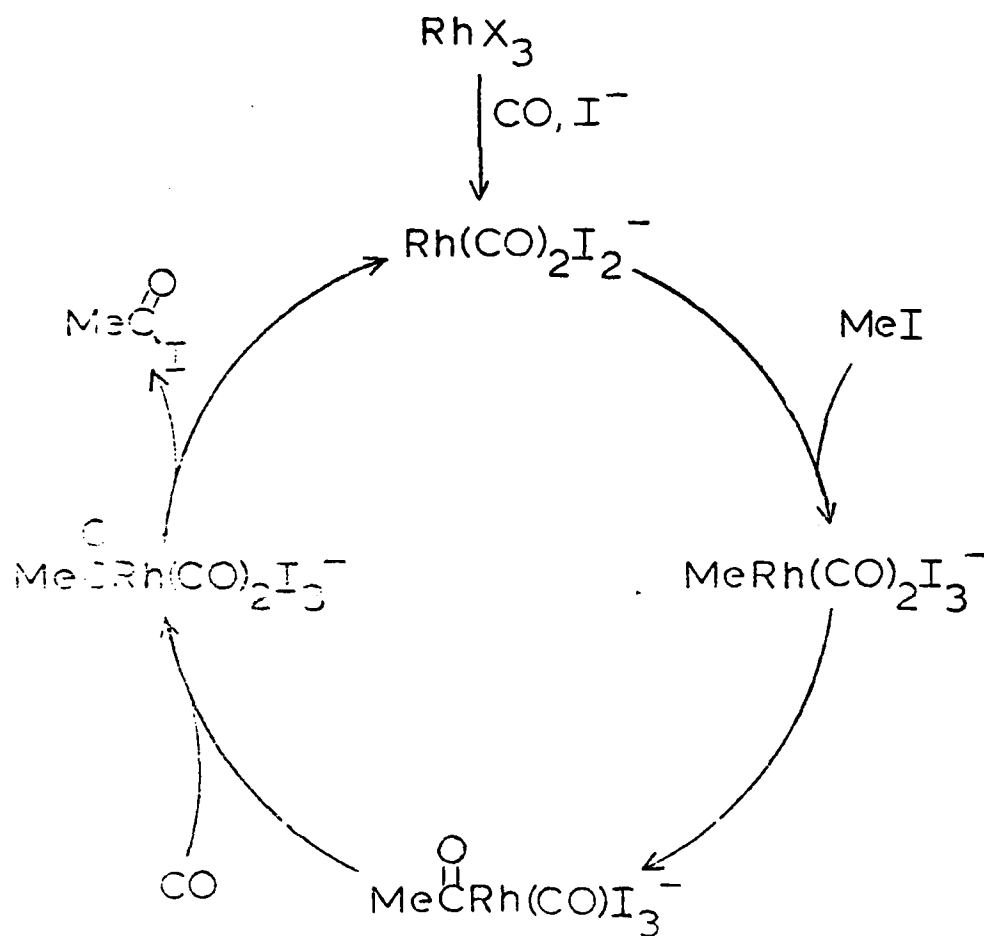
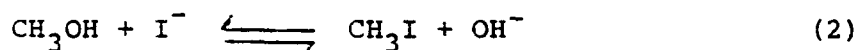


Figure 1. Mechanism of the carbonylation of methanol by $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

Further kinetic studies¹⁴ by Hjortkjaen and Jensen found $k = k_0 \exp (-E/RT)$ where $k_0 = 3.5 \times 10^6$ l/mol sec and $E = 14.7$ kcal/mol. In the presence of excess CO, $[\text{Rh}(\text{CO})_2(\text{I})_3(\text{CH}_3)]^-$ complex inserts CO into the Rh-CH₃ bond, adds CO, and reductively eliminates acetyl iodide. The free acetyl iodide undergoes a substitution reaction with methanol or water, forming methyl acetate or acetic acid, and regenerating free HI.⁽⁶⁾

Methyl iodide can be formed from methanol with a variety of substances⁽¹³⁾ (HI, $\text{CaI}_2 \cdot 2\text{H}_2\text{O}$ and I_2) (eqn 2).



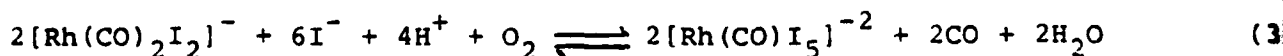
The reaction requires Lewis or Bronsted acid catalysis. The equilibrium lies far to the right⁽⁵⁾ and is attained rapidly at the temperature of the carbonylation process (120°).

Sodium iodide, in the absence of acid, is not an effective promoter for CH₃I formation.⁽⁵⁾ Interest in a solid phase acid catalyst for the formation of CH₃I from NaI is due to the highly corrosive nature of the acidic homogeneous solution.⁽¹⁵⁾ The solid phase acid should retain its acidity within the solid phase thus reducing the corrosive nature of the solution.

RESULTS AND DISCUSSION

Preparation and Characterization of the Catalyst

The rhodium catalyst was heterogenized by reacting ion exchange resins (Bio Rex 9, Dowex 1-X8 or a copolymer of styrene and 4-vinylpyridine alkylated with methyl iodide, forming methyl pyridinium functionalized polymer) with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in the absence of CO and iodide, or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of excesses of these reagents. This in situ catalyst generation was preferred over preliminary supported catalyst synthesis and isolation because of the greater control of the rhodium concentration for each catalytic run. Resins with the yellow color characteristic of the $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ ($\text{X}=\text{Cl}^-, \text{I}^-$) species⁽¹⁶⁾ were obtained from both rhodium precursors. Isolation of the yellow resin was straightforward for the catalyst derived from the rhodium dimer, and its infrared spectrum exhibited CO stretching bands at 1981 and 2065cm^{-1} which are in good agreement with those reported for the tetraphenylarsonium salt of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (at 1988 and 2060cm^{-1} in CH_3COOH).⁽¹⁶⁾ However, isolation of the yellow catalyst derived from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in excess CO and iodide resulted in an immediate decomposition of the catalyst to a red species with a CO band observed at 2040cm^{-1} . This reversible decomposition has been previously reported⁽¹⁶⁾ (reaction 3) and the red product characterized as $[\text{Rh}(\text{CO})\text{I}_5]^{-2}$ (infrared band at $\sim 2040\text{cm}^{-1}$).



The yellow species could be isolated after reimmersing the polymer supported red complex in methanol under CO at room temperature and again filtering the yellow beads in the absence

of excess iodide. Carbonyl bands were observed at 1980 and 2050cm^{-1} in the infrared spectrum of this supported catalyst, again supporting the identification of the supported yellow complex as $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

The rhodium complex is concluded to be ionically bound, and not simply trapped, because in the preparation of the catalyst nearly all of the rhodium is extracted from the solution onto the beads as evidenced by lack of catalytic activity in the filtrate (vide infra).

Catalytic Runs

Catalysts were compared by monitoring the CO pressure drop after demonstrating by NMR, IR and GLC that acetic acid and methyl acetate were the sole products of the catalytic reaction. Data which permit a comparison of the homogeneous and supported systems are contained in Table 1. The rates of carbonylation of methanol for the supported systems are equal, within experimental error, to those for the homogeneous systems as seen by comparison of run 1 with 2 and 3, as well as run 10 with 11. This similarity in rates is an unusual finding for supported catalysts because either the structure of the catalytic species is modified upon heterogenizing or diffusion of the reactants through the polymer to the catalyst becomes rate controlling. Grubbs et al. found inhibition of catalytic reaction rates occurred because of diffusion problems with hydrocarbons containing six or more carbon atoms.⁽¹⁷⁾ The smaller molecules involved in our system ($\text{CO}, \text{CH}_3\text{I}$), even with a much higher gel resin crosslinking (8%) and a poorer swelling

Table 1. Polymer Bound and Solution Catalysts for the Carbonylation of Methanol.

Run	mmoles $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	moles I (source)	time of run (min)	ΔP_{CO} (psi)	additional reagents
1 (H)*	0.190	0.20(HI), 0.03(CH_3I)	68	9	60ml CH_3COOH 60ml CH_3OH 25ml H_2O (designated solvent A)
2 (P)**	0.190	0.20(HI), 0.03(CH_3I)	68	11	solvent A 0.50g Dowex 1-X8(iodo form)
3 (P)	0.190	0.20(HI), 0.03(CH_3I)	68	10	solvent A 2.00g Dowex 1-X8(iodo form)
4 (P)	0.190	0.20(HI), 0.03(CH_3I)	136	20	solvent A 2.00g Dowex 1-X8(iodo form) (same soln as in 3)
5 (H)	filtrate from run 4	0.20(HI), 0.03(CH_3I)	136	5	solvent A (no Dowex)
6 (P)	0.190	0.20(HI), 0.03(CH_3I)	120	15	145ml 60/40 benzene/ CH_3OH 2.00g Dowex 1-X8(iodo form)
7 (H)	filtrate from run 6	0.20(HI), 0.03(CH_3I)	120	1	145ml 60/40 benzene/ CH_3OH (no Dowex)
8 (P)	0.390	0.31(HI)	90	15	30ml CH_3COOH 20ml CH_3OH 5.00g BioRex 9(Cl form)
9 (H)	filtrate from run 3	0.31(HI)	180	0	30ml CH_3COOH 20ml CH_3OH (no BioRex 9)
10(H)	0.380	0.20(HI), 0.03(CH_3I)	68	23	solvent A
11(P)	0.380	0.20(HI), 0.03(CH_3I)	68	22	solvent A 4.00g Dowex (same soln as in 10)

* (H) indicates a homogeneous reaction.

** (P) indicates a polymer supported reaction.

solvent, do not seem to exhibit diffusion controlled reaction rates, as judged from the similarity in the reaction rates for both the homogeneous and supported systems. At least two examples of supported cationic complex systems in which the catalytic activity is different than their homogeneous counterparts have been reported. Wilkinson et al. exchanged a Rh_2^{4+} cation on a Dowex resin and found that in the presence of $(\text{C}_6\text{H}_5)_3\text{P}$ this resin was 1/40th as active as the homogeneous counterpart in the hydrogenation of 1-hexene.⁽³⁾ Intercalated cationic rhodium species have been reported that are twice as effective as the homogeneous catalyst.⁽¹⁸⁾

The equivalence of both the homogeneous and supported catalytic rates supports our earlier conclusion that the same catalytic species is present in both systems. This data also indicates there is no significant decrease in rate from an ion pairing energy change due to increased ionic size from the oxidative addition of CH_3I to the rhodium anion. The delocalization of the $\text{Rh}(\text{CO})_2\text{I}_2^-$ complex's negative charge on oxidative addition may be expected to result in a decreased electrostatic interaction with the polymer support's cationic function, and thus in an energy destabilization in the rate determining step of this reaction.

The rate law for the supported system appears to be first order in $(\text{Rh}(\text{CO})_2\text{I}_2)^-$ in runs 3 and 11 where doubling the concentration of the supported catalyst (by doubling the RhCl_3 and Dowex bead concentrations) resulted in an approximate doubling of the reaction rate. This result suggests that a liquid flow system design in which there is a large catalyst to methanol ratio could prove to be a very effective method for carrying out the reaction. Such ratios are limited in the homogeneous system by catalyst solubility. This apparent similarity of reaction

order in rhodium, as well as the equivalence of the homogeneous and supported catalysts' rates, supports our characterization of the ionically bound species as $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

As evidenced by run 5, leaching of the catalyst did occur with the conditions employed in run 4. To determine the effectiveness of lowering the solvent dielectric on the extent of leaching, runs 6 and 7 were conducted. These indicate that substituting a benzene/methanol solvent (in a 60/40 volume ratio) for the acetic acid/methanol/water solvent, with otherwise identical conditions, results in a drop in leaching from 25% to 7% with little attendant rate reduction. It is important to note runs 8 and 9 demonstrate leaching may be eliminated. Here the polymer weight to solution volume ratio was increased and the dielectric of the solvent decreased (in relation to runs 4 and 5). A catalytic run with the filtrate from run 8 (run 9) resulted in no CO pressure drop, even though twice as much time was allowed for the reaction. This result clearly indicates that leaching in ionically supported catalyst systems may be controlled by adding more polymer support, decreasing solution volume, or changing solvent polarity.

Table 2 contains the results of a series of experiments in which investigations were carried out on the effects of heterogenizing the acid and iodide source. As reported,⁽⁵⁾ NaI cannot be used in place of HI, CH_3I or I_2 (run 12) as a promoter for methyl iodide formation from methanol. The catalytic effect of adding activated molecular sieves (solid phase acid) to the solution of run 12 is demonstrated in run 14.

Thus catalysis of reaction 2 can be carried out by a heterogeneous phase that contains an acid (see Figure 2). A titration of the sieves before and after catalysis establishes that the acidity remains in the heterogeneous phase, thus avoiding the problems associated with high solution acidity. Even with 7.0g of sieves, the rate of CO uptake is much slower than when I_2 or CH_3I was used (runs 18 and 19). This is due to a low concentration of protons from the 7g of sieves. At low $[H^+]$ the rate of carbonylation of methanol is limited by the rate of formation of methyl iodide from sodium iodide. The formation of methyl iodide was verified with both GLC and NMR. An equivalent number of protons from HNO_3 were more efficient at CH_3I formation than the molecular sieve source (run 17 compared to run 14).

When Dowex 1-X8 supported I^- and $[Rh(CO)_2I_2]^-$ was used without a Lewis acid (run 15), no pressure drop was observed, and analysis of the solution showed no CH_3I . However, when 10.0g of sieves were added to a solution of Dowex supported I^- and $Rh(CO)_2I_2^-$ (run 16) catalysis did occur, and the GLC indicated a small amount of CH_3I present in solution. The CH_3I formed must have resulted from diffusion of I^- into the sieves, and illustrates the dynamic nature of Dowex bound I^- .

We have demonstrated the ionic attachment of a rhodium catalyst to a polymer exhibits catalytic rates comparable to the solution analog, and will not leach under suitable conditions. We have also shown that solid phase acids are effective in converting sodium iodide to methyl iodide. More importantly, this study serves to further demonstrate the potential value of ionically supported catalysts in general, and will hopefully spur more work in this neglected area.

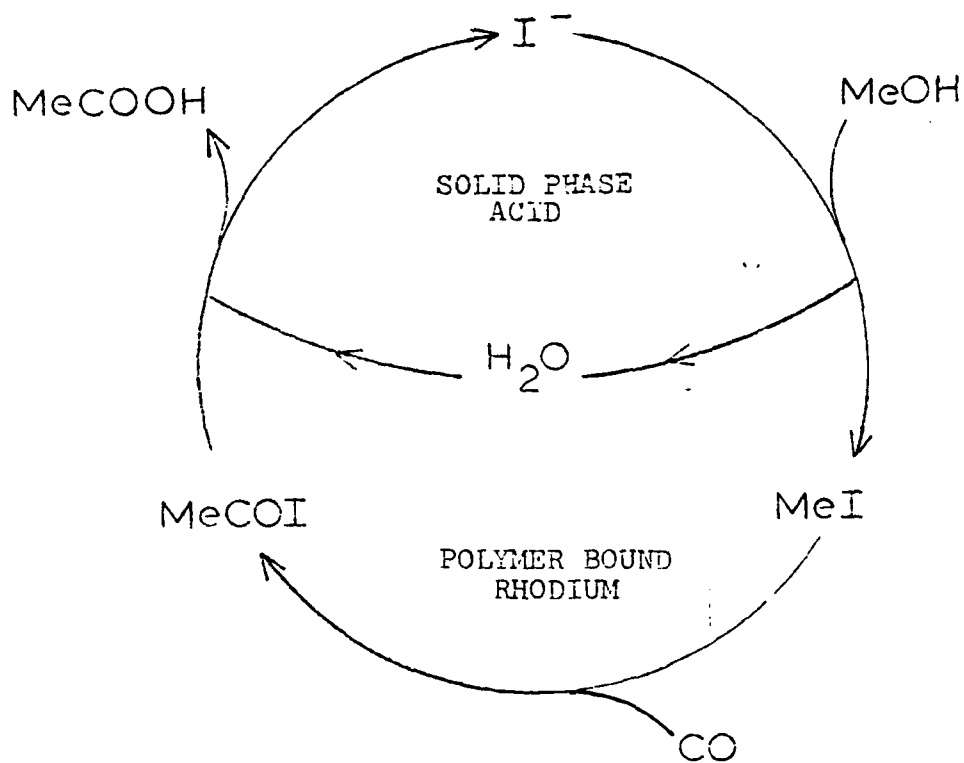


Figure 2. Catalytic cycles; top, solid phase acid catalyzes the formation of CH_3I , bottom, polymer bound $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalyzes the carbonylation.

Table 2. Methanol Carbonylation with Supported Promoters and iodide sources.

Run	<u>mmoles</u> <u>RhCl₃·3H₂O</u>	<u>moles I (source)</u>	<u>time</u> <u>of run</u> <u>(hr)</u>	<u>ΔP_{CO}(psi)</u>	<u>additional reagents</u>
12	0.190	0.040(NaI)	10	0	100ml CH ₃ OH
13	0.190	0.040(NaI)	12	1	100ml CH ₃ OH 2.0g sieves
14	0.190	0.040(NaI)	21	7	100ml CH ₃ OH 7.0g sieves(21mmole H ⁺)
15	0.28	0.011(on Dowex beads)	24	0	60ml CH ₃ COOH 60ml CH ₃ OH 42ml H ₂ O 4.00g Dowex (iodo form)
16	0.190	0.013(on Dowex beads)	25	5	100ml CH ₃ OH 5.00g Dowex (iodo form) 10.0g sieves
17	0.190	0.040(NaI)	21	12	100ml CH ₃ OH 21mmole HNO ₃
18	0.190	0.040(I ₂)	10	12	100ml CH ₃ OH
19	0.190	0.160(CH ₃ I)	3	28	50ml CH ₃ OH 2.00g Dowex (iodo form)

EXPERIMENTAL

MATERIALS:

The methyl iodide (Eastman Kodak), rhodium chloride trihydrate (Alfa Products), hydriodic acid and sodium iodide (Mallinckrodt) and all solvents were of reagent grade and used without further purification.

The iodide form of the Dowex 1-X8 anionic exchange resin (200-400 mesh) was prepared by stirring soxhlet extracted (4/1 Dioxane/ H_2O) chloride forms beads with a 10-fold excess of NaI in an acetone/ H_2O solvent for two days, further soxhlet extracting, and oven drying at $70^\circ C$ (analysis: 34.6% I, 0.3% Cl). Polystyrene bound methyl pyridinium iodide was prepared by the addition of polystyrene bound pyridine (1.0g) to a stirred solution of benzene (20ml) and methyl iodide (5.0ml). This was refluxed for 23 hours, collected by suction and air dried. Bio-Rex 9 was used as the chloride form after soxhlet extracting for two days.

The catalyst, $[Rh(CO)_2I_2]^-$, was prepared in situ before each run from $RhCl_3 \cdot 3H_2O$, I^- and CO in the presence of all other solvents and reagents used in a particular run, at a temperature of either $25^\circ C$ or $120^\circ C$ depending on the speed of its formation. For example when using HI catalyst formation occurred in 30 min at $25^\circ C$, while with NaI it required ≈ 5 hrs at $120^\circ C$. Catalyst formation was indicated by its characteristic yellow color.

The solid phase acid was generated from Linde Molecular Sieve Catalyst Base LZ-Y62 powder on heating at $400^\circ C$ for 3 days, resulting in the loss of ammonia from the ammonium counter-ion function of the sieves, and leaving behind caged protons. The time of heating controls the acidity of the sieves, and we were able to drive off nearly stoichiometric

quantities of ammonia, generating a solid phase with approximately 2-3 mmoles H^+ /g sieves as determined by titration with a sodium hydroxide solution.

APPARATUS:

All catalytic runs were carried out in a 500ml Parr pressure bottle equipped with a 200 psi Marsh pressure gauge and gas inlet-outlet tube for filling and purging. The bottle-copper tubing interface was sealed by a tightly clamped silicone rubber stopper. No pressure drop occurred from the sealed system in 24 hrs on pressurization to 120 psi at either RT or 120°C. The apparatus was checked for leaks every five or six runs to insure there were no spurious pressure drops.

Contributions to ΔP_{CO} from both CO concentration and solution vapor pressure changes during the reaction were considered and found to be negligible for all pressure drops. At the temperature employed for the runs (120°C) the steady-state concentration of CH_3I was achieved in a negligible amount of time (except when using NaI), as determined from identical pressure drops for consecutive runs of the same solution.

CATALYTIC RUNS:

A typical catalytic run was carried out as follows; to a 500ml Parr pressure bottle was added 0.100g $RhCl_3 \cdot 3H_2O$, 4.00g Dowex 1-X8 (iodide form), 60ml CH_3COOH , 60ml CH_3OH , 25.0g HI, 2.0ml CH_3I and a magnetic stirring bar. The bottle was connected to the pressure apparatus previously described and purged six times with 100 psi CO at room temperature over a period of 30 minutes. The solution was then stirred until it

turned orange or light yellow (30 minutes to three hours depending on amount of Dowex resin present), the pressure lowered to precisely 80 psi CO, equilibrated, the apparatus placed in a preheated oil bath at 120°C, and vigorously stirred. After 68 minutes in the 120°C bath the apparatus was removed and immediately place in an ice-water bath for 15 minutes with continued stirring for fast reaction termination. The final pressure was read one hour later at room temperature.

The GLC spectra were recorded on a Varian Model 940 FID instrument at 55°C or 80°C using a one meter, 1/16 inch I.D. copper column packed with Chromasorb P supported diethylene glycol adipate. All infrared spectra were recorded as Nujol Mulls on a Perkin-Elmer Model 599B, and the NMR on a Varian 390. The production of acetic acid and methyl acetate was confirmed by NMR, GLC and IR, as well as from their characteristic odors and the CO pressure drops. Methyl iodide formation was confirmed by both GLC and NMR.

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